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Synthetic Organic Chemicals

PUBLISHED BY THE

EASTMAN KODAK COMPANY, ROCHESTER, NEW YORK

VOL. IV PUBLISHED JULY, 1931 No. 5

Flotation Reagents

THE use of flotation methods for the separation and concentration of ores has increased very rapidly in the last ten years. Although the physics and chemistry of the process are not entirely understood, recent studies have aided materially in determining the proper conditions for the most efficient use of the method. Government figures for 1928, the latest available, show that 59 million tons of ore were treated by the flotation process in that year.

This process depends on the action of air bubbles, which, passing upward through a liquid, have the power of attracting and carrying particles of mineral matter with them. While it is conceivable that this surface tension phenomenon in certain cases would allow a separation of the mineral constituent of the ore from the gangue using only air and water, it has been found that the addition of small amounts of chemicals increases this desirable effect very markedly. These chemicals have been classified roughly according to their effects as activators, regulators, frothers, collectors or promoters, and depressors. Most of the reagents used come under one of these headings although they may also have some additional influence.

One of the principal requirements of the process is that the mineral should have a metallic lustre. For this reason, as would be expected, copper ores are especially adaptable to flotation methods, and of the 59 million tons of ore treated in 1928, 47 million were copper-bearing. Lead and zinc ores can also be handled successfully. Some non-lustrous minerals through treatment with "activators" acquire a thin coating which makes them act as though they had a true metallic lustre. Lead carbonate ores when activated with small amounts of sodium sulfide are very much improved and have flotation properties more like galena. Sphalerite (zinc sulfide) is a poor floater, but if the wet ore mixture is treated with a little copper sulfate, the surface properties are changed so effectively that it is easily carried by the bubbles.

"Regulators" are inorganic chemicals exclusively. They include sodium hydroxide, soda ash, lime, and sulfuric acid. Their principal use is in regulating the hydrogen-ion concentration; and, as a mildly alkaline solution seems to work best in most cases, lime is used in the greatest amounts. Ammonia has also been suggested as being more advantageous for certain minerals.

"Frothers" are added to make the air bubbles more permanent, and of these, pine oil and cresylic acid are most often used. Although over 4,000 tons of these two reagents were used in 1928, only a few ounces are needed for each ton of ore. Pine oil gives a thin, rather transient froth while cresylic acid yields stronger bubbles which are more permanent. Even tougher froths can be

obtained by using higher coal tar distillates; however, the mineral separation is less selective. Cresylic acid is a tar distillate containing various mixtures of cresols and xylenols. The most active constituent has been found to be meta-cresol while the xylenols as a group are apparently less valuable than the cresols. Propyl phenol is as efficient as meta-cresol but is not present to any great extent in ordinary cresylic acids. Other organic reagents used as frothing agents are ortho-toluidine and xylidine.

Frothing in flotation machines is secured by mechanical agitation or aeration. In one of the pneumatic types, the air is forced through a rotating rubber cylinder perforated with thousands of small holes. As the wet mixture is aerated, the mineral particles are carried with the froth to the top where the concentrate is scraped off and dried.

The degree of fineness to which the ore is originally ground is very important, although in many instances discarded tailings from previous mining operations have been found ideally suited to reworking by the flotation process.

While the frothers provide an abundance of stable bubbles, "collectors" or "promoters" influence very markedly the capacity of these bubbles to carry mineral particles. Less than one ounce of a collector per ton of ore will increase the mineral recovery from an original 31% to 93%. This group of reagents has received the most study and many interesting compounds have been investigated. One of the best known is potassium ethyl xanthate although some of the other xanthates are more effective and often used. Within certain limits, increasing the length of the aliphatic chain improves the efficiency. For instance, the mineral recovery in a series of tests with equal amounts of ethyl, iso-propyl, and secondary butyl xanthates was 85%, 90% and 94% in the order named. The higher cetyl ester, however, was less effective. Ethyl xanthate is the ethyl ester of dithiocarbonic acid. It is a much better collector than the corresponding monothiocarbonic ester. The dithiophosphates are also used as promoters in relatively large amounts. In addition, they exert some frothing action as well. Differing from the xanthates, phenolic compounds of dithiophosphoric acid may be obtained as readily as the alkyl esters. Other collector agents include creosotes, thiocarbanilide, alpha-naphthylamine, and even mercaptobenzothiazole.

"Depressors" are compounds, mainly inorganic, which are added to reduce the tendency of the gangue materials to be carried along with the froth. The cyanides are the most common depressors, although silicates and sulfites are sometimes used.

In practice, the reagents are added almost automatically although frequent checks are made of the mineral content in the concentrate and the tailings as a guide to the amounts required. If, as is often necessary, a series of flotation machines is used, the different units may vary somewhat in the proportion of reagents added. This is especially true when two minerals are to be selectively separated from the gangue.

On account of the importance of metallic lustre, the flotation process is largely confined to metallic sulfide ores, although recent studies are rapidly extending its application. Manganese ores, as well as the lead carbonate mentioned previously, are now being concentrated by this process. Bauxite and non-metallic products such as barytes and coal are also treated by flotation methods. As in all mining operations, the location and composition of the ore largely determine the process to be used. Because of the small amounts of reagents needed and the high efficiency obtainable, especially with low-grade ores, flotation methods are gaining rapidly over other methods of concentration.

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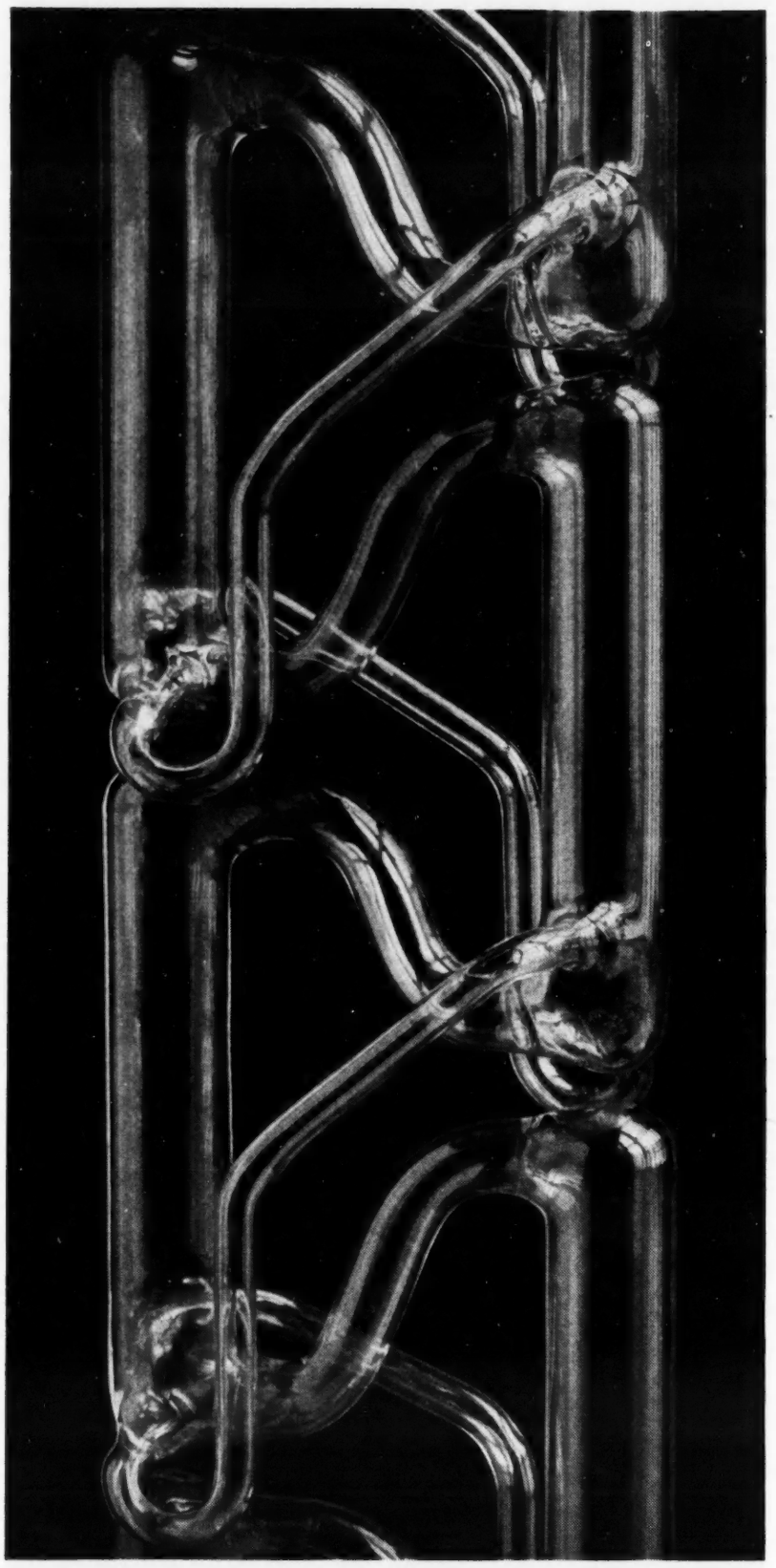
An Improvement in the Bubbler-Type Distilling Column

THE operation of the Clarke-Rahrs type of bubbler column, described in the October, 1929, issue of this publication, can be improved by a slight change in the liquid return tube. If the narrow overflow tube is connected to the unit below with a small upward bend in the form of a J, a trap is formed which prevents any of the vapor escaping through the tube instead of bubbling through the liquid. The change overcomes the difficulty that was sometimes encountered when the distillation was pushed too rapidly. In this slightly modified form there is no chance for the vapor to proceed upward in the column without it first being washed by the liquid condensate collected in the bottom of each unit.



Section of bubbler-type distilling column

This type of distilling column is very efficient and more rugged than would ordinarily be expected. In addition, the number of units can be varied to suit the conditions encountered. Since many of our products are purified by distillation, we use a large number of these columns in which the number of units varies from 3 to 13. Some of the larger ones used with 22-liter flasks are more than a meter high and are made with tubes 25 mm. in diameter. Their effectiveness is illustrated in the dehydration of acetic acid. A product containing less than 0.1% water can be obtained from the glacial material in one distillation without the use of a dehydrating agent. In the purification of aliphatic bromides and chlorides, the various isomers are readily separated from one another as well as from the corresponding alcohols.

Eastman Organic Chemicals as Analytical Reagents

XX Reagents for Beryllium.

CURCUMIN

Kolthoff, J. A. C. S. *50*, 393 (1928)

The reagent is a 0.1% solution of curcumin in alcohol. In weakly alkaline solutions this indicator is absorbed by the beryllium hydroxide with the formation of an orange-red color. If the solution contains beryllium alone, to 10 cc. are added only one drop of indicator, one-half cc. of 4 N ammonium chloride, and 6 to 8 drops of 4 N ammonia. A solution containing 50 mg. of beryllium per liter gives a red flocculent precipitate; with 1 mg. per liter the color is orange-red.

Potassium, sodium, lithium, calcium, and barium do not interfere. Magnesium decreases the sensitivity somewhat but 1 mg. per liter of beryllium can be detected in the presence of 1 gm. of magnesium per liter. Aluminum and iron interfere but may be removed by first treating the slightly acid solution with an excess of sodium fluoride and filtering. The filtrate is made just alkaline and tested as described above.

8-HYDROXYQUINOLINE

Lundell and Knowles, Bureau of Standards Jnl. Research *3*, 91 (1929)

Aluminum and beryllium can be easily separated with 8-Hydroxyquinoline in spite of the similarity between them. A slightly acid solution of the two metals is warmed to 60° and treated with an excess of an acetic acid solution of the reagent. Twice normal ammonium acetate is added until a permanent precipitate is obtained. After settling, the aluminum compound is filtered off and washed with cold water. The beryllium in the combined wash water and filtrate is precipitated with ammonia, filtered, and ignited to the oxide.

New Eastman Organic Chemicals

Nearly 100 new chemicals have been added to our stock since the first of the year. The most recent additions include the following, all of which are either manufactured or purified in our own laboratories:

n-Amyl n-Caproate
Benzalacetophenone Dibromide
Boron Triacetate
p-Chlorothymol
Dianisalacetone
5.7-Dibromo-8-hydroxyquinoline
Dicinnamalacetone
Di-m-nitrobenzalacetone
2.4-Dinitromesitylene
Dipiperonalacetone
Di-p-tolualacetone
Di-m-tolylurea
Ethoxyethyl Maleate
Furfuralacetophenone
Furfural Diacetate
Furfuraldoxime
Furoamide
Furonitrile
Furoyl Chloride
Furylacrolein
Furylacrolein Oxime
Furylacrylamide
Furylacryloyl Chloride
o-Methoxydiphenyl
Methyl o-Iodobenzoate
8-Methylquinoline
m-Nitrobenzalacetophenone
m-Nitrobenzalfurfuralacetone
p-Nitrobenzyl Acetate
p-Nitrobenzyl Alcohol
o-Nitrophenetole
Salicylaldoxime
Trichloro-tert.-Butyl Acetate
m-Tolylurea
Tri-o-cresyl Thiophosphate
Tri-m-cresyl Thiophosphate
Tri-p-cresyl Thiophosphate
Triphenyl Thiophosphate
2.4.6-Trinitromesitylene
Vanillinacetone